Appl Nanosci (2014) 4:103–112
DOI 10.1007/s13204-012-0178-5

ORIGINAL ARTICLE

Cation exchange resin nanocomposites based on multi-walled carbon nanotubes

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Received: 17 October 2012 / Accepted: 14 November 2012 / Published online: 2 December 2012

Abstract Carbon nanotubes (CNTs) are of great interest due to their potential applications in different fields such as water treatment and desalination. The increasing exploitation of multi-walled carbon nanotubes (MWCNTs) into many industrial processes has raised considerable concerns for environmental applications. The interactions of soluble salt with MWNCTs influence in the total salt content in saline water. In this work, we synthesized two cation exchange resins nano composites from polystyrene divinylbenzene copolymer (PSDVB) and pristine MWNCTs. The prepared compounds were characterized using infra red spectroscopy, thermal stability, X-ray diffraction, and electro scan microscope. Also, the ion capacities of prepared cation exchange resins were determined by titration. Based on the experimental results, it was found that the thermal stability of prepared nanocomposites in the presence of MWNCTs increased up to 617 °C. The X-ray of PSDVB and its sulfonated form exhibits amorphous pattern texture structure, whereas the nano composite exhibits amorphous structure with indication peak at 20° and 26° for the PSDVB and MWCNTs, respectively. The ion-exchange capacity increased from 225.6 meq/100 g to 466 mg/100 g for sulfonated PSDVB and sulfonated PSDVB MWNCTs-pristine, respectively.

Keywords Ion exchange resin · Desalination · CNTs · Pristine multi-walled carbon nanotubes · Suspension polymerization

Introduction

Ion exchange resins are polymers capable of exchanging particular ions within the polymer with ions in a solution passed through them. Synthetic resins used primarily for purifying water and other applications including separating out of some elements. In water purification, ion-exchange resins are usually used to soften the water or to remove the mineral content altogether. The advantages of the ion-exchange resins process are a long life of resins, cheap maintenance, etc. In addition, the process is very environmentally friendly because it deals only with substances already occurring in water. Ion-exchange resin comprises polystyrene and is the most famous polymer or resin used for water demineralization.

The structure, high aspect ratio, and chemical bonding properties of carbon nanotubes (CNTs) combine to produce a material with electro-mechanical properties that can be exploited in polymer composites and a variety of light-weight, high-strength structural materials (Song et al. 2008; Coleman et al. 2006; Yang et al. 2008). The wide range of possible applications of CNTs has been a driving force for the commercialization and industrial-scale production of high-quality single-walled (SW), double-walled (DW) and

Electronic supplementary material The online version of this article (doi:10.1007/s13204-012-0178-5) contains supplementary material, which is available to authorized users.

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multi-walled carbon nanotubes (MWCNTs), and as a result these materials are now readily available for incorporation into intermediate and final products as CNT/polymer composites. However, there are significant challenges in the preparation of CNT/polymer composites, particularly concerning the need for ensuring adequate interfacial adhesion between the CNTs and polymers as required, thus ensuring a uniform distribution of CNTs throughout the composite and avoid agglomerate formation (Li et al. 2008). Furthermore, unless the interface is carefully engineered, poor load transfer between nanotubes (in bundles) and between nanotubes and surrounding polymer chains may result in interfacial slippage and compromise the mechanical strength of the nanocomposite. Approaches to addressing these challenges include chemical modification and functionalization of the CNTs (O'Connell et al. 2001), surfactant treatment (Islam et al. 2003), and polymer wrapping (Yang et al. 2007). CNTs are of great interest due to their potential applications in different fields of science and technology; they offer a combination of mechanical, electrical, and thermal properties that no other material has displayed before (Coleman et al. 2006). The integration of CNT/polymer composites has been focused on the improvement of mechanical and electrical properties of the matrix (Ramanathan et al. 2005; Frankland et al. 2003; Eitan et al. 2006); however, in order to take advantages of such properties CNTs have to be both compatible and intimately dispersed within the polymer host. Nevertheless, due to strong Vander Waals forces, CNTs have a great tendency to self-aggregate (Hill et al. 2002; Park et al. 2005). Several strategies have been employed to improve both compatibility and dispersion of CNTs into polymer matrixes (Lee et al. 2006). Several studies have shown that in situ polymerization is a reliable method for obtaining CNT/polymer composites (Funck 2007; Zhao et al. 2005), with the advantage of improving interfacial interaction to impart compatibility and to maximize CNT dispersion. In particular, the techniques of polymerization in dispersed media have been successfully applied to encapsulate nanomaterial's into polymer matrixes, with the most successful being miniemulsion polymerization, which provides proper conditions to integrate either organic or inorganic nanoparticles with the polymer matrix (López-Martinez et al. 2007; Erdem et al. 2000). Nevertheless, considering the typical aspect ratios of CNTs (length/diameter) encapsulation by miniemulsion polymerization seems to be quite difficult; it would be like trying to introduce a baseball bat into a baseball ball. Reports have shown that in composites obtained via miniemulsion polymerization, the interaction between CNTs and polymer particles has been basically the adhesion of the polymer particles along the surface of the CNTs (Park et al. 2005; Vandesvorst et al. 2006; Ham et al. 2005). Therefore, miniemulsion polymerization or even conventional emulsion polymerization seems to be not the proper techniques to encapsulate CNTs; thus, some other options should be explored (Xie et al. 2005).We consider improvements of polystyrene divinylbenzene (PS-DVB) by adding CNTs, which might bring superior thermal stability, high strength, and flexibility. Also, the cross-linked structure of such PS-DVB co polymer yields a network structure with relatively low chain mobility.

In this study, we synthesize MWCNTs/divinylbenzene copolymer, nano composite resin by suspension polymerization. Benzoyl peroxide (BPO) was used as the initiator. Infra red spectroscopy, thermal stability, X-ray diffraction (XRD), and electro scan microscope of prepared composite were characterized. The ion capacities of prepared cation exchange resins were determined by titration.

Experimental

Materials

Styrene (Merck), BPO were supplied (Merck, as cross-linking agent), and used without further purification, dichloromethane, acetone, trimethylamine, Toluene, from Egyptian market and were used as received. MWNCTs was synthesis in EPRI in Nano lab purity of 95 wt% an average diameter of 15 nm and lengths ranging from 0.5 to 1 μm with most of the materials closer to 1 μm. Surfactant, Hydroxyl propyl cellulose (HB) (Merck), and sodium dodecyl benzene sulfonate (SDS).

Methods

Synthesis of polystyrene (PS)

Suspension polymerization of polystyrene seeds was carried out in 250 mL round bottom flask at 75 °C for 6 h. 1 wt% of hydroxyl propyl cellulose was dissolved in distilled water solution (150 mL) and loaded into the reactor. 14 g of styrene and 0.12 g of BPO were added, and the mixture solution was homogenized at 600 rpm using mechanical stirrer to form the stable microspheres. The polymerization products were rinsed with ethanol and centrifuged repeatedly to remove any non-reacted styrene and HB. The PS microspheres were then dried in a vacuum oven at room temperature for 48 h (Bak et al. 2011; Zhong et al. 2011; Matheel et al. 2007).

Synthesis of polystyrene divinylbenzene copolymer beads

The PS-DVB copolymer beads were prepared by suspension polymerization technique. The initiator (BPO) was

dissolved in the monomers (styrene and divinylbenzene) and the diluents. BPO leading to the formation of free-radicals on both CNTs and PS-DVB, which produced internal polymer-grafted nano tubes with the desired distribution in the resin. This mixture was added to the suspension solution formed by dissolving one of cellulose derivatives in deionized water. Then, all were poured in 1 L four neck flasks fitted with a mechanical stirrer, nitrogen inlet, condenser, thermometer, and pressure indicators, and the reaction mixture was heated to 75 °C and was allowed to proceed at this temperature for 6 h and at 90 °C for another 18 h under nitrogen atmosphere with constant stirring at 300 rpm. After that, the copolymer beads were filtered and washed with dilute HCl solution and sufficient quantity of hot water and extracted with acetone, dried at 150 °C and sieved. Then, they were washed first with acetone and finally with pure methanol (Ghaderi et al. 2006; Sherrington 1998).

Synthesis of PS-DVB and PS-DVB–CNT beads

Two grams polymer of PS seeds was placed in 500 mL three neck flask. Then, the emulsified solution containing 30 mL SDS aqueous solution (0.2 %, w/v) was added and stirred overnight. Afterwards, another emulsified mixture consisted of 30 g organic compounds and 250 mL HB aqueous solutions (1 %, w/v) were prepared by an Ultrasonic Compact Hielscher UP200Ht (200 W, 26 kHz) and poured into the flask for swelling. The organic compounds consisted of styrene, divinylbenzene, MWCNTs, toluene, BPO and SDS having toluene equaled to the sum of styrene and divinylbenzene, while BPO was only 1.5 % of the sum (w/w). The amount of SDS was 0.25 % of the HB aqueous solution (w/v). The amount of MWCNTs 1 % (w/w) was attempted to prepare PS-DVB-CNT particles. After 24 h the temperature was increased to 70 °C under nitrogen atmosphere and left for another 24 h. Subsequently, the resulting beads were washed successively with hot water and alcohol. Then, the beads were extracted with toluene for 48 h. After washing and drying, the resulting particle size of the stationary phase was about 50 Mm (Zhong et al. 2011; Hielscher et al. 2005).

Sulfonation of resin

Sulfonation of styrene–divinylbenzene Copolymer and nanocomposites was performed in solution with acetyl sulfate as the sulfonating agent. Acetic anhydride reacts with sulfuric acid to form acetyl sulfate (sulfonating agent) and acetic acid (by product) which removes excess. The sulfonation reaction produces sulfonic acid substituted to the Para-position of the aromatic ring in the styrene block of the polymer. A 10 % (w/v) solution of styrene–divinylbenzene copolymer (20 g) in methylene chloride (200 mL) was prepared. The solution was stirred and refluxed at approximately 40 °C, while a specified amount of acetyl sulfate in methylene chloride was slowly added to begin the sulfonation reaction. Acetyl sulfate in methylene chloride was prepared prior to this reaction by cooling 150 mL of methylene chloride in an ice bath for approximately 10 min. Certain amount of acetic anhydride with acetic anhydride in excess of a 1:1 mol ratio was mixed. This solution was then allowed to return to room temperature before addition to the reaction vessel. After approximately 5 h, the reaction was terminated by slowly adding 100 mL of methanol. The reacted polymer solution was then precipitated with deionized water. The precipitate was washed several times with water and methanol, separately, and then dried in a vacuum oven at 50 °C for 24 h. This washing and drying procedure was repeated until the pH of the wash water was neutral (Ganguly and Bhowmick 2008; Elabd and Napaden 2004).

Characterization of the MWCNT nanocomposite resin

Characterization of functional groups on the synthesized resin was done by Fourier transform infrared (FTIR) spectroscopy (Nicolet 8700, ThermoScientific, USA) with an attenuated total reflection (ATR) unit (ZnSe crystal, 45 °C). Resin samples were rinsed with deionized water and then dried in a vacuum oven before analysis. FTIR spectra of the resin were recorded in transmittance mode over a wave number range of 4,000–650 cm^{-1} at 25 °C.

The surface morphology of the resin was investigated by scanning probe microscope (SPM) (Digital Instruments Dimension 3100, Veeco, and Woodbury, NY, USA) and scanning electron microscopy (SEM) (Superscan SSX-550, Shimadzu Co., Kyoto, Japan). The thermal stability of resin PS-DVB/MWCNT microspheres was analyzed by Thermo gravimetric analysis (TGA, Q50, TA instruments, K), from 20 to 600 °C scan temperature and at a heating rate of 10 °C/min under air atmosphere. XRD was used to examine the crystallinity/crystal structure and phase constituents of samples. The XRD measurements were performed with powders packed completely in the holder of a RigakuD/MAX RINT 2500 X-ray diffractometer operated at 40 kV and 100 mA. The incident wavelength was Cu K $\lambda = 1.5406$ Å and the detector moved step by step ($2\theta = 0.05°$) between 10° and 90°. The scan speed was 40 min. The ion-exchange capacity for prepared resin was determined by titration process. Titrations were carried out by dissolving 150 mg of PSSO3H in 15 mL of methanol. The sulfonation degree (x) was expressed as mole percentage of the sulfonated styrene repeating units, PS-xSO3H. Homogenizer, Ultrasonic Compact Hielscher

UP200Ht (200 W, 26 kHz) Stand was used for sonication of MWCNTs in HB aqua solution.

Results and discussion

FTIR analysis

Figure 1 exhibits FTIR spectra of the pristine MWNCTs and shows a broad peak at ~2,984.91 cm^{-1}, which refers to the O–H stretch of the hydroxyl group. The presence of hydroxyl and carboxyl groups on the pristine MWCNTs could be due to the partial oxidation of MWCNTs surfaces during the purification by the manufacturer. The FTIR spectra of polystyrene as shown in Fig. 2 appear stretching absorption peaks at 3,024.38 cm^{-1} for alkenyl C–H, and two peaks at 752.02, 905.37 cm^{-1} for disubstituted benzene. Absorption peaks of PS-DVB in Fig. 3 show absorption peaks at 3,021.97–2,916.43, 1,442.99, 1,491.26 and 1594.82 cm^{-1} that correspond to the stretching and bending aromatic–CH_2–, –CH–bands, respectively.

The absorption peaks of PS-DVB sulfated represent broad stretching vibration S=O band around 1,123.63 cm^{-1} as shown in (Fig. 4). Whereas the presence of vibration band at 1,499.39 cm^{-1}, this may be due to the weakness of the skeletal of benzene ring and this might be due to higher percentage of sulfonated portion in comparison to polystyrene part in the cross-linked core. Also, the broad band at 1,640.36–1,716.00 cm^{-1} range is due to hygroscopic nature of this material. Figure 5 represents absorption peaks of the composite PS-DVB-p-MWCNTs and shows medium alkenyl C–H peak at 3,023.71 cm^{-1}, and medium stretch band at 2,918.11 cm^{-1} that may be for methylene (–CH_2–); also, a strong bands at 754.99, 537.64 cm^{-1} could be represent benzene disubstituted ring. Absorption peaks for PS-DVB-p-MWCNTs sulfated represent S=O stretching vibration around 1,170.89 cm^{-1} as shown in (Fig. 6). The vibration band appears at 1,447.64 cm^{-1} due to the weakness of the benzene ring and higher percentage of sulfonated portion in comparison to polystyrene part in the cross-linked core. The broad band in 1,695.61 cm^{-1} range is due to hygroscopic nature of this material.

Characterization by TGA

The TGA of the pristine MWCNT in (Fig. 7) show decomposition temperature between 500 and 650 °C. The temperatures at maximum weight loss appear at 600 °C for the pristine MWCNT. The weight loss on the pristine MWCNT is correlated with the decomposition of MWCNT via oxidation, as the characteristic combustion temperature of disordered carbon usually emerges at around 400 °C (Couteau et al. 2003). Therefore, TGA could be a measure of the degree of functionalization of CNT (Dyke and Tour 2003). The decomposition of the organic moieties occurs first before that of carbon.

The TGA analysis of PS-DVB in (Fig. 8) showed decomposition temperature in two steps, the first step started at 266 °C and ending at 466 °C, meanwhile the second step started at 466 °C and ending at 600 °C; this means that about 99.8 % of total sample decomposed and the remaining is 0.11 %. The TGA analysis of nano composite PS-DVB pristine MWCNT in Fig. 9 exhibited two decomposition phases, one of them started at 266 °C and ending at 450 °C, the second start at 450 °C and ending at 617 °C; this means that about 97.76 % of total sample decomposed and the remaining is 3.22 %, the slight increased in the remaining weight attributed to the presence of pristine MWCNTs.

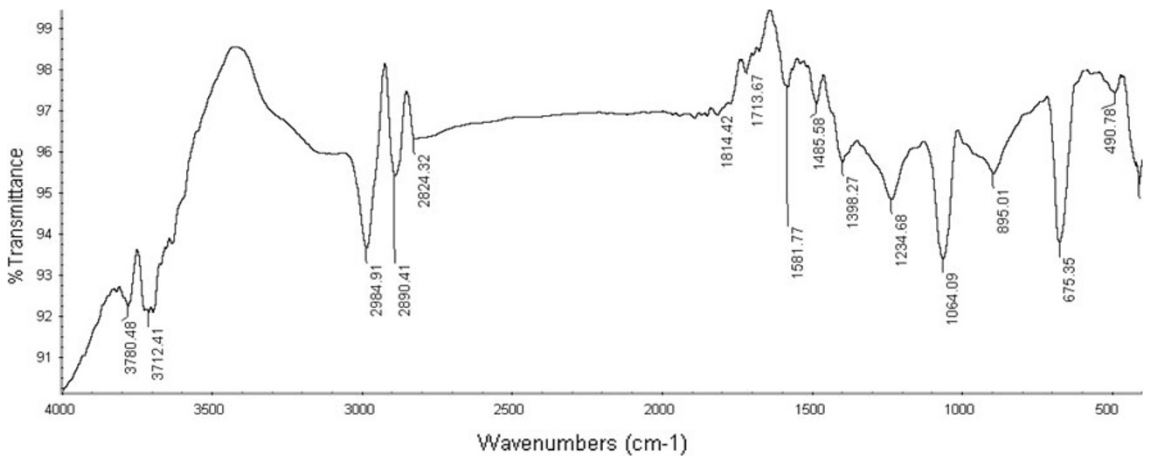

Fig. 1 FTIR of pristine MWCNTs

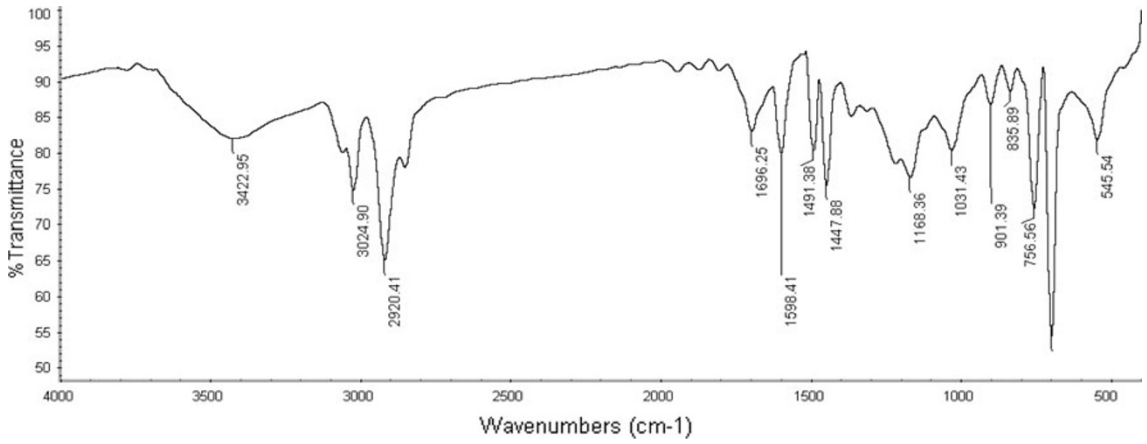

Fig. 2 FTIR of polystyrene resin

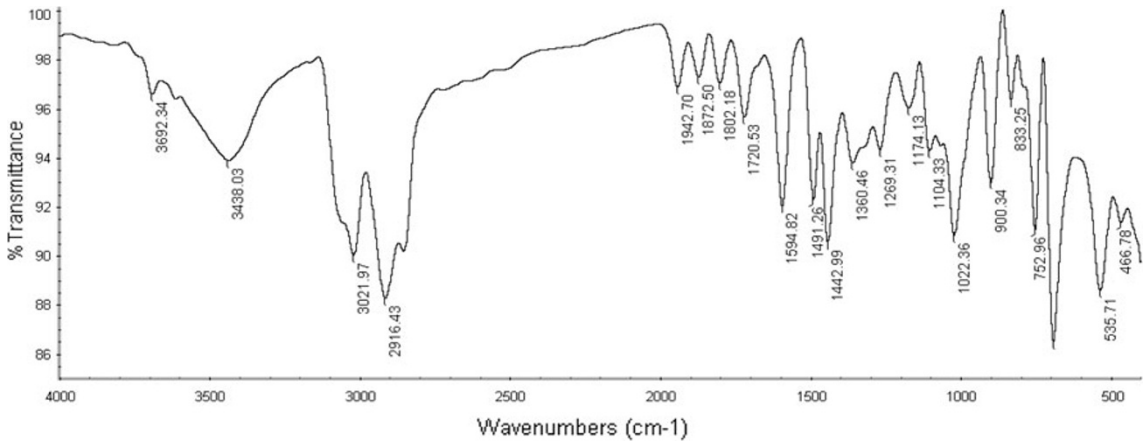

Fig. 3 FTIR of polystyrene divinylbenzene resin

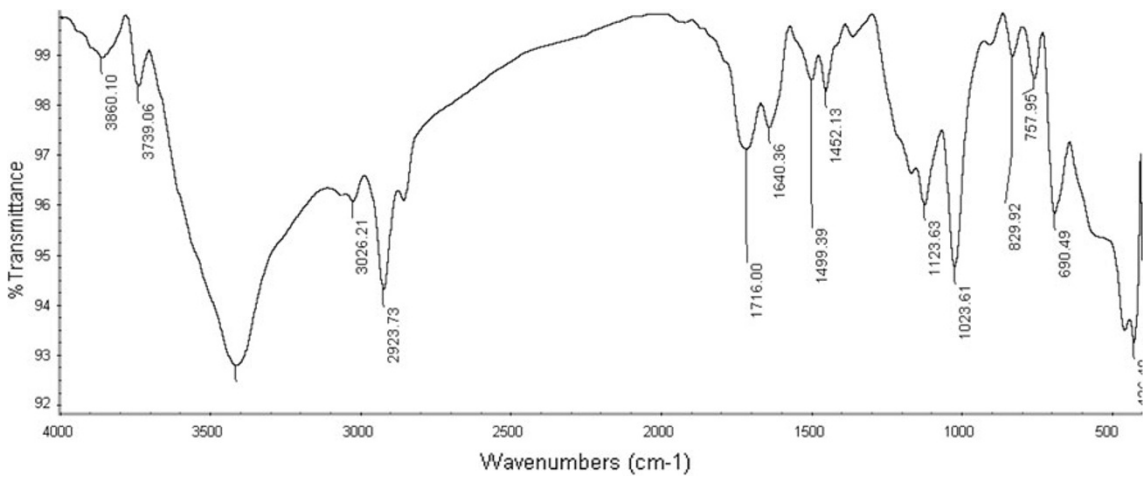

Fig. 4 FTIR of sulfonated polystyrene divinylbenzene resin

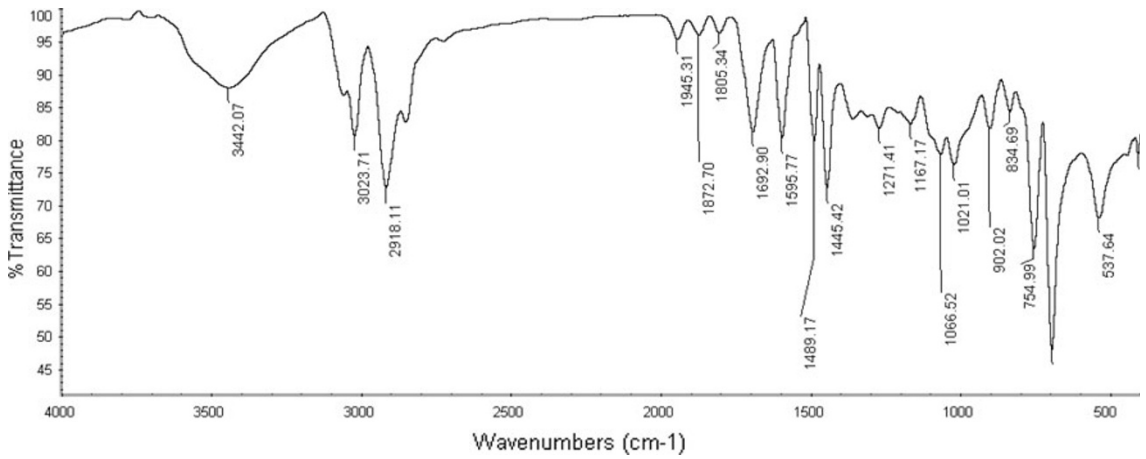

Fig. 5 FTIR of polystyrene divinylbenzene with (1 wt%) p-MWCNTs resin

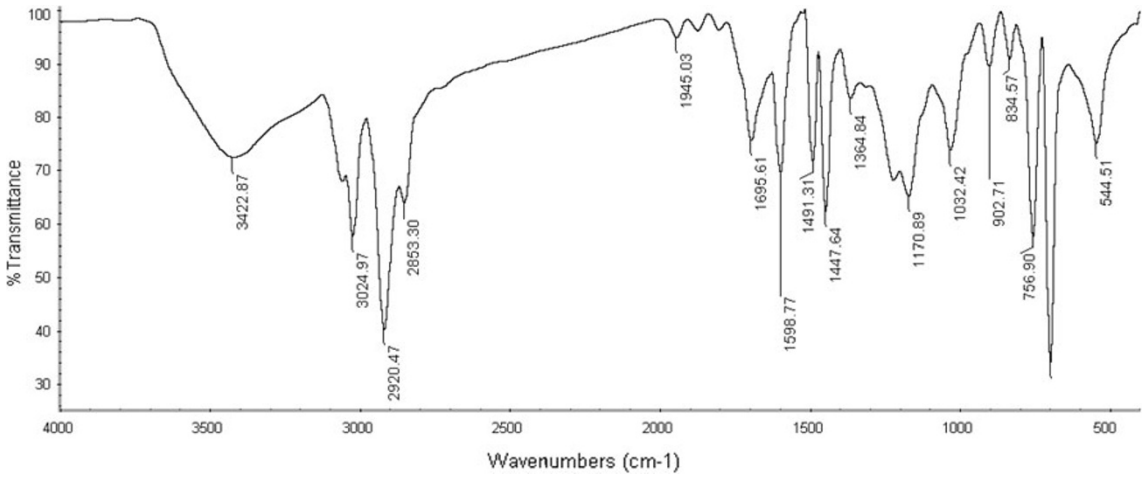

Fig. 6 FTIR of sulfonated polystyrene divinylbenzene with (1 wt%) p-MWCNTs resin

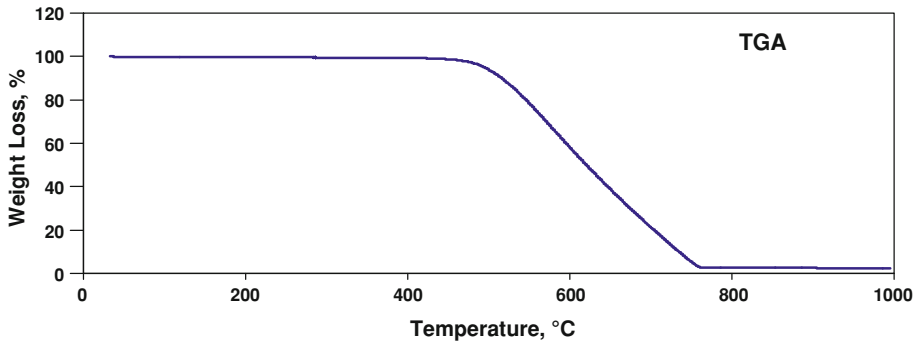

Fig. 7 TGA analysis of p-MWCNTs

X-ray analysis

Figure 10 shows the XRD patterns of pristine MWCNTs. In this figure, the significant diffraction pattern of the pristine MWCNTs is appeared at 2θ of 25.3°. The 2θ peaks are corresponded to (002) reflection planes or known as interlayered spacing between adjacent graphite layers, respectively. The (002) reflection peaks was observed at the same 2θ values in pristine MWCNTs diffractions.

With respect to specialized diffraction pattern of prepared resin (Figs. 11, 12), it is clear that the pattern exhibits amorphous structure with indication band at 20° at 2θ of traditional prepared resin. Meanwhile, the diffraction pattern of resin containing pristine MWCNTs (Fig. 10)

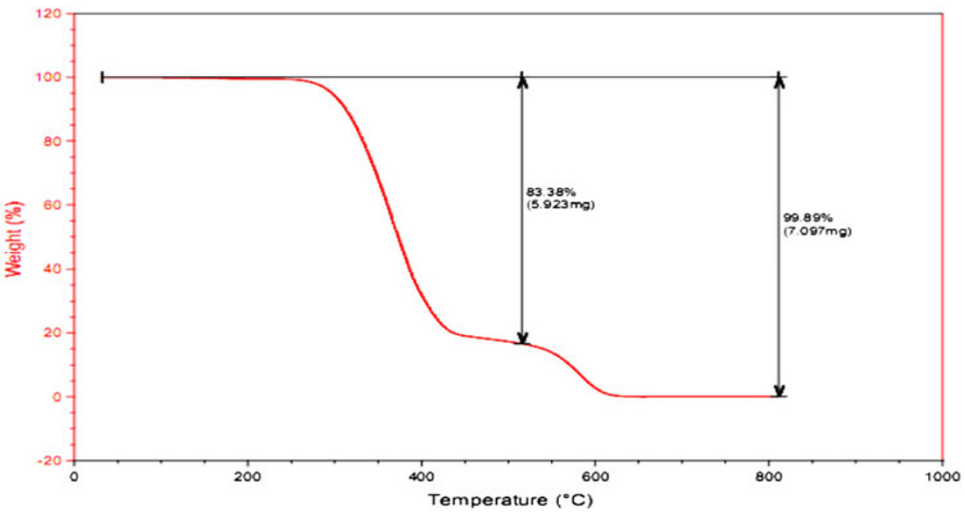

Fig. 8 TGA analysis of polystyrene divinylbenzene resin

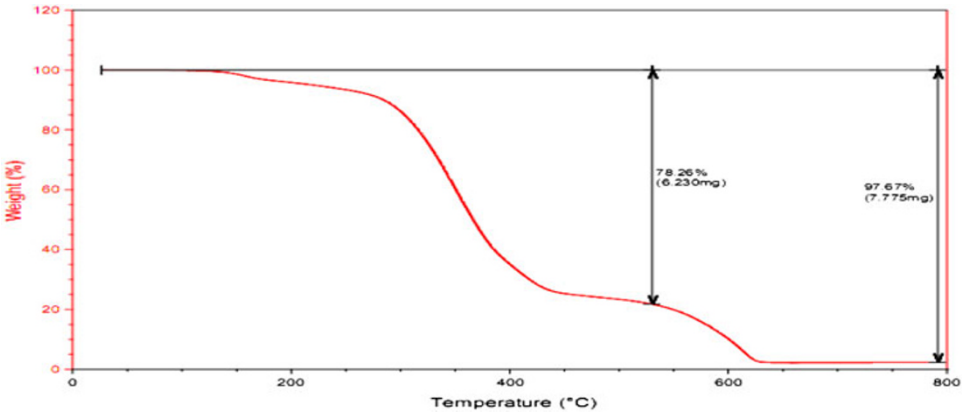

Fig. 9 TGA analysis of polystyrene divinylbenzene with (1 wt%) p-MWCNTs resin

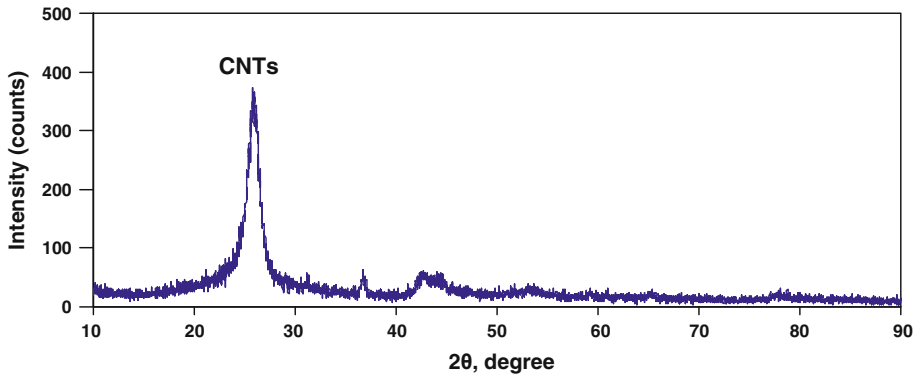

Fig. 10 X-ray diffraction of p-MWCNTs

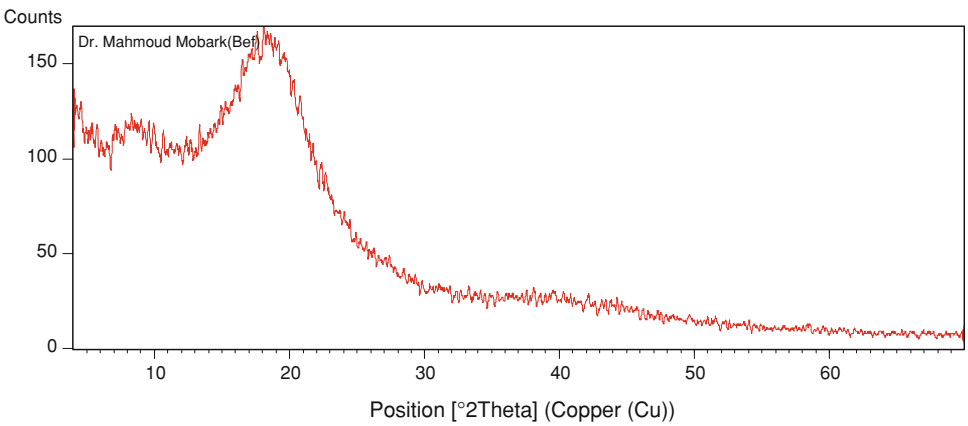

Fig. 11 X-ray diffraction of polystyrene divinylbenzene resin

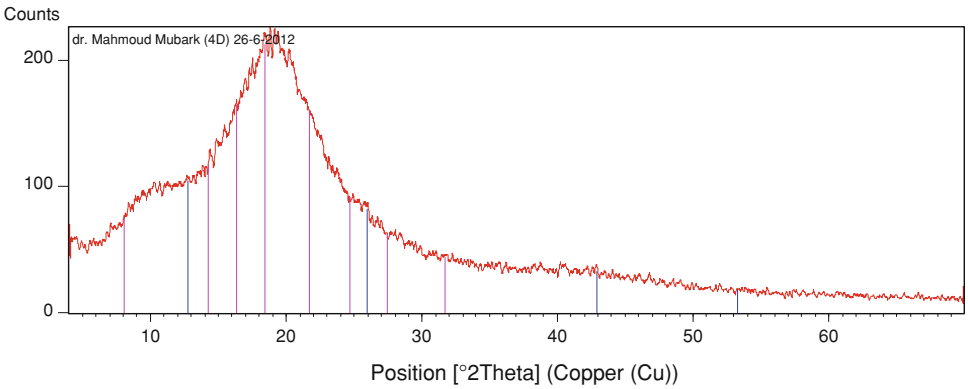

Fig. 12 X-ray diffraction of polystyrene divinylbenzene with (1 wt%) p-MWCNTs resin

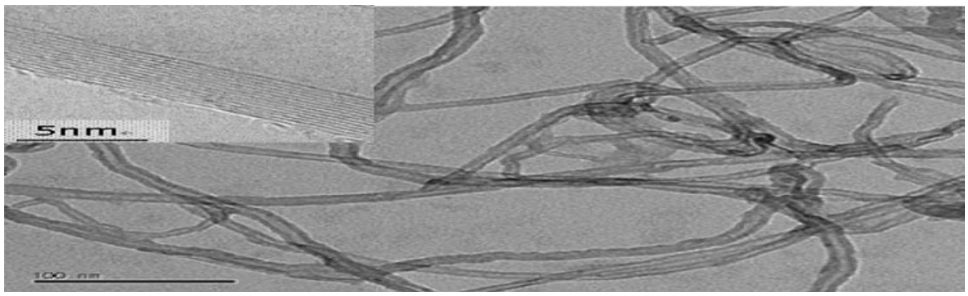

Fig. 13 TEM of p-MWCNTs resin

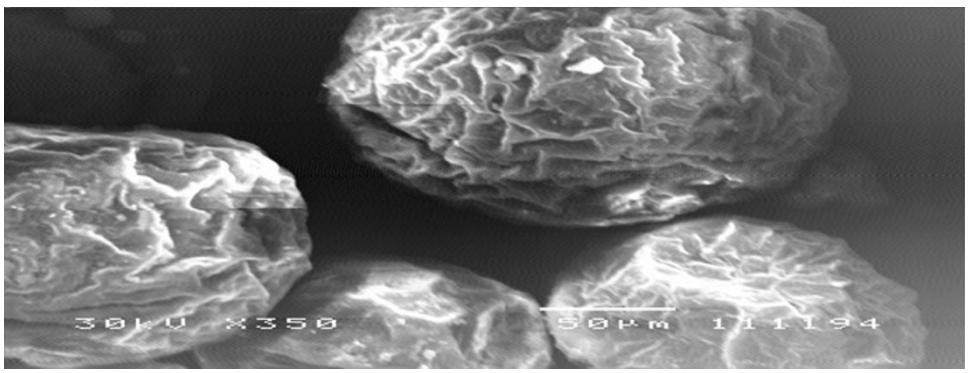

Fig. 14 SEM of polystyrene divinylbenzene resin

appears a significant band near 26° at 2θ with very small band and this may be due to the small concentration of MWCNTs and formation of nanocomposite.

TEM and SEM analysis

From the TEM image shown in Fig. 13, it was observed that the pristine CNTs (A, B) have different diameters and closely entangle with each other due to their strong self-cohesive nature. Also, such figure exhibits clear picture for the outer radius of individual MWCNTs.

The morphology of the microspheres was observed using field emission scanning electron microscopy (FESEM, S-4200, Hitachi, Japan) at an accelerating voltage of 15 kV. In this respect, the prepared resins were pre-coating with a homogeneous Pt layer by ion sputtering (E-1030, Hitachi, Japan). Figures 14 and 15 show the particle size and surface morphology of PS-DVB particles in absence and presence of MWCNTs, it is observed that with the addition of MWCNTs, the surface areas and pore volumes of the particles decrease for PS-DVB and PS-DVBMWCNTs, respectively, but the pore sizes of the particles were increased for the same rank, respectively, which means that the pore structures were changed with the addition of MWCNTs. This can be explained during the synthesis of the PS-DVB-CNT particles; the MWCNTs were shortened and incorporated into the PS-DVB particles. In addition, there was no extra reactive site between PS-DVB and MWCNTs, and a few of the MWCNTs were embedded inside the particle, whereas most of them could be seen on the surface of the particles. This means that the porosity and the outer structures of the PS-DVB-CNT

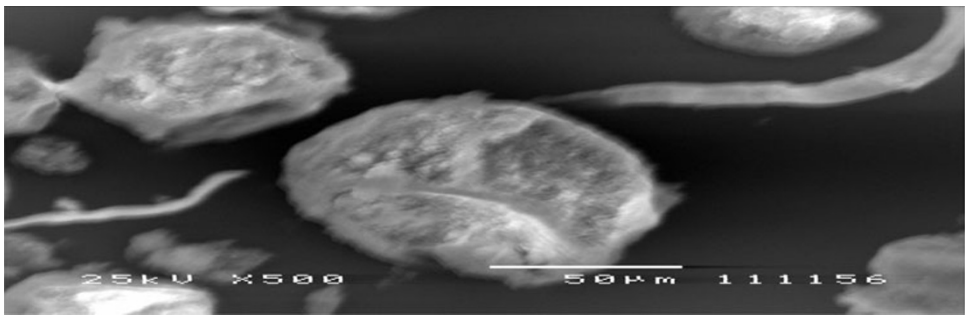

Fig. 15 SEM of polystyrene divinylbenzene with (1 wt%) p-MWCNTs resin

particles were changed, which contradicts what happened in corresponding particles containing oxidized MWCNTs (Zhong et al. 2011).

Capacity

During the titration of prepared resins (PS-DVB SO_3H and PS-DVBMWCNTs SO_3H) with 0.01 mol L^{-1} NaOH solutions in methanol, it is observed that the cationic exchange capacity of PS-DVB MWCNTs particles (oxidized one) is highly increased twice with respect to PS-DVB SO_3H that recorded 2,256 meq/100 g; meanwhile, the prepared resins containing MWCNTs in oxidized form achieved cationic exchange capacity values of 446.6 meq/100 g. Although the PS-DVB MWCNTs SO_3H containing only 1 % of its weight CNTs.

Conclusion

The addition of MWCNTs to PS-DVB resin to form nanocomposite structure improved the mechanical properties of these resin and their ability to exchange ions in sea water with high capacity of exchange. The pristine MWCNTs improved resins hydrophilic properties and increased their cation exchange capacity from 225 to 446.6 meq/100 g CNTs due to the formation of different functional groups on the CNTs surface. X-ray analysis of traditional resin (PS-DVB) exhibits amorphous structure with indication band at 20°. Meanwhile, the diffraction pattern of resin containing pristine MWCNTs appears a significant and very small band at 26°; this may attributed to the small concentration of MWCNTs and formation of nanocomposite. Our results are in agreement with that described in previous works. The morphology of the microspheres was observed using FESEM which show that a few of the MWCNTs were embedded inside the particle, whereas the most of them could be seen on the surface of the particles. This means that the outer structures of the particles were changed and so was the porosity.

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